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The Working Domain in Reactive Extrusion. Part II: The Effect of the Polymerization Rate

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This article describes the influence of the polymerization rate on the working domain of a counter-rotating twin-screw extruder used as a polymerization reactor. The rate of polymerization was varied by changing the maleic anhydride (Mah) content in the feed, which consisted of styrene, n-butylmethacrylate, and maleic anhydride. It appeared that the Mah content influenced the operating window of the extruder. Higher Mah percentages resulted in higher throughputs and a decreased dependence on the extruder parameters. On the basis of these results, a new theory concerning reactive extrusion was developed, which resulted in a diagram that is useful in optimizing the extruder, when it is used as polymerization reactor. In addition to the effect of Mah on the process, its effect on product properties was studied.

INTRODUCTION

The copolymerization of styrene with monomers, such as maleic anhydride and methacrylates, is studied thoroughly. The importance of the copolymerization with methacrylates stems from the fact that the polymer finds applications in speciality areas, such as in the manufacturing of recording tapes and toners for photocopiers (1, 2). The copolymer of St-Mah finds applications in waxes and emulsifiers when it concerns a low molecular weight polymer. The high molecular weight materials are mainly used as engineering plastics, which are mostly rubber modified. The styrene-maleic-anhydride copolymers are interesting not only from an industrial point of view, but also from a scientific point of view, because after polymerization, an almost perfect alternating copolymer is obtained (3, 4).

In this study, the extruder is used as a polymerization reactor. The main advantage of the extruder over traditional polymerization reactors is the ability of the extruder to work without a solvent. Moreover, the extruder provides, even at a high viscosity, good mixing and heat transfer. In recent years, several investigations showed that the extruder can be used as a reactor for homopolymerization and copolymerization (5–8). In this paper, special attention is focused on the effect of the polymerization rate on the process of reactive extrusion. The rate of polymerization is changed by changing the Mah content in the monomer feed.

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THE COUNTER-ROTATING TWIN-SCREW EXTRUDER

The counter-rotating twin-screw extruder used in this study is closely intermeshing. This implies that the channel of one screw is blocked by the flight of the other screw. The extruder can therefore be considered a series of C-shaped chambers, in which material is transported towards the die. The theoretical throughput equals the maximum volumetric displacement, which is equal to the number of C-shaped chambers transported per unit time multiplied by the chamber volume:

$$Q_{th} = 2mNV_c \tag{1}$$

where m is the numbers of thread starts, N is the screw rotation rate and V_c is the volume of a C-shaped chamber. Because of mechanical clearances, the formed chambers are not completely closed. Leakage flows cause interaction between the chambers. The real volumetric throughput is therefore given by:

$$Q = Q_{th} - Q_l \tag{2}$$

In most extrusion processes, the extruder is starve-fed. As a result, the extruder is not completely filled. When the feed is a liquid, one can observe two zones in the extruder. Near the feed zone, the chambers are not completely filled; near the die, the extruder is completely filled. The length of the fully filled zone is determined by the pressure needed to overcome the die pressure. As long as the fully filled zone is smaller than the total extruder length, the throughput can be

increased. A more extensive explanation of counter-rotating twin-screw extruders is given by Janssen (9).

This study describes the extruder as a polymerization reactor. A theory about reactive extrusion is developed by Ganzeveld *et al.* (5). The extruder is also simulated as polymerization reactor, based on the same principles (10). The theory concerning reactive extrusion is schematically given by the "Interaction diagram," which is shown in *Fig. 1*. The diagram shows quantitatively the influence of the several extruder parameters on, for example, the conversion. The parameters that can be adjusted are double enclosed. The diagram can be very helpful in understanding the behavior of the extruder in certain situations. However, our experiments show some situations in which the interaction-diagram fails. For example, the interaction diagram considers the throughput as a primary parameter that can be set freely at any value in the normal extruder operating window. In steady state, the pressure profile will adapt itself to the throughput, viscosity, and die resistance. However, our experimental results indicate limitations of the throughput being a primary parameter. To describe the experimental results better, a new theory is developed, which takes into account limitations in throughput and several other effects and evaluates the usefulness of the interaction diagram.

THE REACTION KINETICS

The bulk copolymerization of styrene (St) with n-butyl-methacrylate (BMA) or maleic anhydride (Mah) is a free radical addition polymerization. This means that after initiation, a polymer chain grows in a rather short time. Owing to a termination reaction, the polymer chain is excluded from further reaction. The kinetic scheme for homo- and copolymerization is given by Bamford (11). For homopolymerization, the polymerization rate equals:

$$v_p = k_p \sqrt{\frac{fk_d[I]}{k_t}}[M] \tag{3}$$

The molecular weight of the polymer formed may change during radical polymerization. At a certain time, the molecular weight of the newly formed homopolymer is given by:

$$M_{mom} = \frac{\text{chance of propagation}}{\text{chance of termination}} = \frac{k_p[M\cdot][M]}{k_t[M\cdot]^2} W_m$$

$$= \frac{k_p}{\sqrt{fk_dk_t}} \frac{[M]}{\sqrt{[I]}} W_m \tag{4}$$

The theory for homopolymerization and copolymerization can be extended to the polymerization in which three components react (11). In that case, the propagation rate consists of nine steps. The ratio of the amount of A and B that react in a certain time is given by the following equation:

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]} \frac{\left(\frac{[A]}{r_{21}r_{31}} + \frac{[B]}{r_{21}r_{32}} + \frac{[C]}{r_{23}r_{31}}\right)\left([A] + \frac{[B]}{r_{12}} + \frac{[C]}{r_{13}}\right)}{\left(\frac{[A]}{r_{12}r_{31}} + \frac{[B]}{r_{12}r_{32}} + \frac{[C]}{r_{13}r_{32}}\right)\left([B] + \frac{[A]}{r_{21}} + \frac{[C]}{r_{23}}\right)} \tag{5}$$

in which:

$$r_{12} = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_{21} = \frac{k_{22}}{k_{21}} \text{ etc.} \tag{6}$$

The polymerization of St-BMA is the starting point of this research. When a certain part of the BMA is replaced by Mah, a faster polymerization is obtained, which has turned out to be a good tool for investigating the effect of the reactivity on the extruder performance. The terpolymer obtained by polymerizing St-BMA-Mah is comparable to terpolymerization St-Mah-MMA, as described by Schmidt-Naake (12). They found that the terpolymerization equation accurately predicts the terpolymer composition when based on the reactivity ratios of the several binary subsystems. Moreover, they found a strong increase in initial polymerization rate when Mah was added to a mixture of St and MMA. This increase diminished when the reaction proceeded, but over the whole conversion range the mixture that contains most Mah resulted in the highest rate of polymerization.

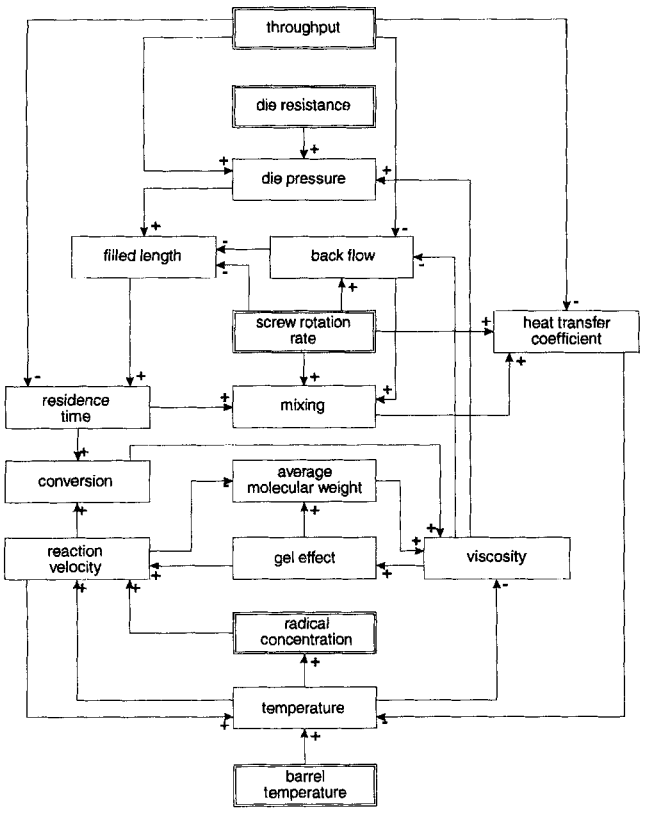

Fig. 1. Interaction diagram.

THE REACTION KINETICS OF ST-BMA AND ST-BMA-MAH AT HIGH TEMPERATURES

Until now, most studies concerning the copolymerization of St with n-BMA or St-Mah have been performed at moderate temperatures. Because the temperature in the extruder ranged from 120 to 160°C, additional experiments were necessary to investigate the kinetics of the polymerization.

The copolymerization of styrene with n-BMA and the terpolymerization of St-BMA-Mah were studied by using differential scanning calorimetry (DSC). The copolymerization and terpolymerization were considered as a pseudo homopolymerization in order to investigate the effect of replacing BMA by Mah. The terpolymerization was not described completely, as this was not the goal of this research.

For the copolymerization of St with BMA, the reactivity ratios were determined at $r_1 = 0.40$ and $r_2 = 0.86$ with St as monomer A (13). It appeared that the copolymerization was faster than the homopolymerization of St, but slower than the homopolymerization of BMA or the copolymerization of St-Mah. The copolymerization of St with Mah is a remarkable polymerization. Although Mah hardly polymerizes and the polymerization of styrene is rather moderate, the copolymerization of the two components is very fast. The reactivity ratios of this copolymerization are around $r_1 = 0.03$ and $r_2 = 0.00$ (14). The subsystem BMA-Mah has not been investigated in the literature. Studies of a comparable subsystem, MMA-Mah, reveal that mainly MMA polymerizes, as a result of which composition drift occurs during polymerization (15, 16).

The effect of Mah on the rate of polymerization was investigated by means of a mixture that was used during reactive extrusion. The results of DSC experiments at 140°C are shown in *Fig. 2*. It can be seen that the addition of Mah led to a much faster polymerization.

The question that now arises is whether the reaction is accelerated only in the low conversion range, or the polymerization is accelerated over the whole conversion range. One possible reaction mechanism is that styrene first reacts very fast with Mah, after which the remaining styrene polymerizes rather slowly with BMA. In that case, a mixture of two polymers is formed. Another possibility is that styrene mainly reacts with Mah, but that in the low conversion range also some BMA will react. As a result of this, Mah will be present during a larger part of the polymerization, leading to a higher reaction rate in a larger conversion range. Therefore, the polymerization rate, which is given by the quantity $k_p/\sqrt{k_t}$, is determined quantitatively by DSC experiments. *Table 1* shows the results of these calculations. These DSC-experiments were performed at 130°C and only 1 initiator was used [10 mmole Trigonox C (an Akzo-Nobel trade mark) per mole styrene]. The addition of Mah led to a strong increase in polymerization rate compared with the copolymerization of St-BMA, but the increase diminished when the reaction proceeded. However, Mah increased the polymerization rate in a larger conversion range than would be expected if St reacts with Mah only in the beginning of the polymerization. After the addition of 20% Mah, the increase in reaction rate was more than a factor of 4 (the lower value at 30% conversion was due to the fact that at high Mah concentrations the polymerization started before the desired reaction temperature of 130°C was achieved. This implied that the value for the reaction rate at 30% conversion corresponded to a lower temperature than 130°C). The results obtained by the DSC experiments were comparable with those obtained by Schmidt-Naake (12) for the St-MMA-Mah system. The DSC experiments showed that mainly the St-Mah-copolymer will be synthesized in the low conversion region, but during the whole polymerization some Mah will present in the monomer mixture, resulting in a higher reaction rate during the whole polymerization.

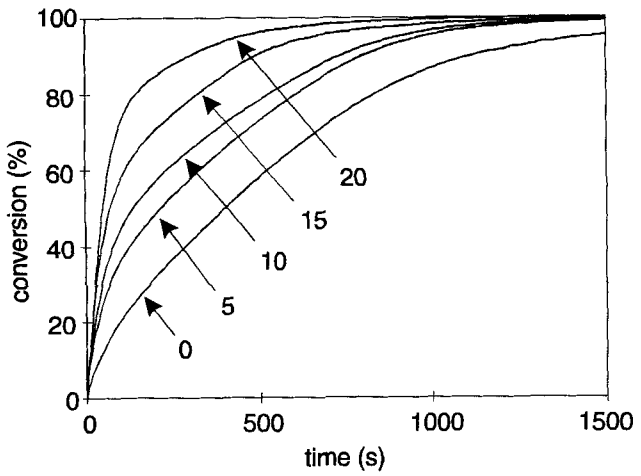

Fig. 2. The influence of Mah on the rate of polymerization. The number at the arrow indicates the percentage of Mah added.

THE EFFECT OF MAH ON THE POLYMER MELT VISCOSITY

The viscosity of a fluid describes the ratio between the shear stress and the shear rate:

$$\eta = \frac{\tau_{xy}}{\dot{\gamma}} \tag{7}$$

in which the shear rate is defined as:

$$\dot{\gamma} = -\frac{dv_y}{dx} \tag{8}$$

The ratio between the shear stress and shear rate is constant for Newtonian fluids. Generally, polymer melts are not Newtonian fluids. This means that the ratio of the shear stress and shear rate is not con-

Table 1. $k_p/\sqrt{k_t}$ ($l^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$) at Different Conversions, Temperature 130°C.

% Mah	At 30% Conversion	At 40% Conversion	At 50% Conversion
0	0.18	0.20	0.23
5	0.27	0.24	0.24
10	0.42	0.41	0.36
15	0.59	0.55	0.48
20	0.35	0.91	0.91

stant, but dependent on the shear rate. The ratio is called the apparent viscosity η_s.

The rheology of the polymer was studied using a capillary viscometer. The measurements were performed in a high pressure capillary apparatus (Rheograph 2003, release 2.1, Göttfert Werkstoff Prömaschinen GmbH). The capillary used had a length of 3 cm, a diameter of 1 mm, and an exit angle of 180° (installed die roundhole 30/1.0/180). The temperature at which the viscosity was determined was 140°C. The measurements were performed at constant pressure. The characteristics of the samples used are given in *Table 2*. In the calculation of the apparent viscosity, we applied the Rabinowitsch correction.

Figure 3 shows the shear rate vs. the apparent viscosity. It can be seen that the effect of 15% Mah is about a factor of 100 in apparent viscosity. This means that Mah increases the polymer melt viscosity significantly.

FEATURES OF THE EXPERIMENTAL SETUP

The extruder used in this study was a counter-rotating closely intermeshing twin-screw extruder with a screw diameter of 40 mm and an L/D of 15. The uniform screw had a pitch of 24 mm. The extruder had four heating zones and a heated die. The die resistance could be adjusted. The initiator and the monomer mixture could be fed separately to a static mixture that is directly connected to the feed zone of the extruder. The monomer mixture could be heated in a stirred tank reactor in order to dissolve all the Mah in the liquid monomers styrene and BMA.

The monomer mixture consisted of 50 mole% styrene. The other 50 mole% consisted partly of n-butyl-methacrylate and partly of maleic anhydride. The initiators used were the same as in a previous study (13). The standard screw rotation rate was 28 rpm (= 0.47 s^{-1}). The standard temperature profile was 120-120-130-140-145°C; the steeper temperature profile was 120-130-140-150-160°C. The standard reciprocal die resistance was 7.4×10^{-11} m^3. In *Table 3*, the actual extruder settings of the experiments that are outlined in the *Figures* are given.

The conversions of the samples collected at the die end of the extruder were determined gravimetrically. The molecular weight of the product was determined by gel permeation chromatography as in previous studies (13, 17). Sometimes, a small part of the terpolymer did not dissolve in the THF, which means that only the molecular weight of the soluble part could be measured.

Table 2. Characteristics of the Samples Used in the Viscosity Measurements.

% Mah	M_n (kg/mol)	M_w (kg/mol)
0	43	99
5	45	105
10	47	103
15	58	143

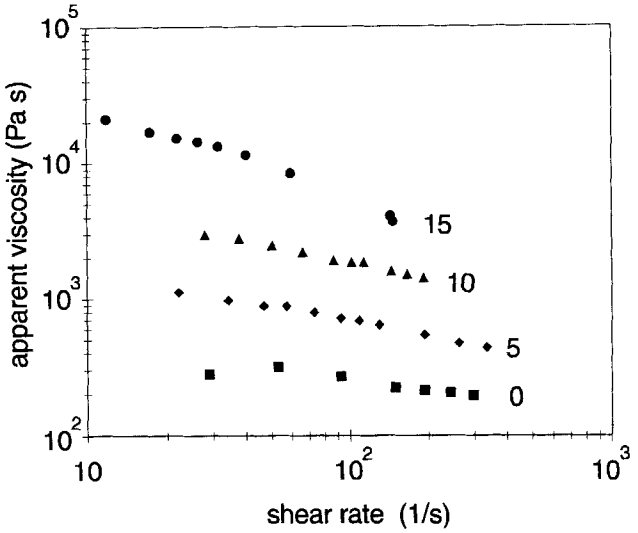

Fig. 3. The apparent viscosity vs. the shear rate.

RESULTS

The Extruder Experiments With No Mah Added

The polymerization of St with n-BMA was rather slow. As a result of the low polymerization rate, the extrusion process was rather difficult to perform. A high die resistance was needed to obtain a high conversion. Owing to the obligatory high die resistance, the extruder became completely filled with liquid at a very low maximum throughput of 7 g/min.

An increase in screw rotation rate or a decrease in die resistance led to a decrease in conversion because of a reduction in residence time. The influence of the die resistance was larger than the screw rotation rate (*Fig. 4*).

The Effect of Mah on the Product Properties

The styrene-n-butyl-methacrylate copolymer is a homogeneous polymer. Although the reactivity ratios indicate that some composition drift is likely to occur, the polymer formed was completely transparent. No phase separation occurred. When maleic anhydride was added to the reaction mixture, the polymer became pale white, indicating some sort of phase separation, although this separation could not be observed under an optical microscope.

One effect of replacing BMA by Mah was an increase in reaction rate. As shown in *Equation 4*, an increase in reaction rate (the ratio $k_p/\sqrt{k_t}$) results in an increased molecular weight. Since the reaction rate of the terpolymerization decreases with the conversion, the polymer formed in the high conversion range will have a lower molecular weight. This results in an increase in the ratio of M_w and M_n of the polymer.

At standard conditions, the results as shown in *Fig. 5* were obtained. The weight average molecular weight increased from 100 to 170 kg/mol, although the increase was significant only if a high percentage (more than 10 mole%) Mah was added to the mixture. The

Table 3. Extruder Settings.

Figure	[I] (mmol/mol St)	Mah (%)	T (°C)	Q (g/min)	K (10^{-11} m^3)	N (s^{-1})
4■	8	0	120–145	6	var	0.47
4◆	8	0	120–140	5	7.4	var
5	8	var	120–145	7–13	7.4	0.47
6	var	15	120–145	16	1.7	0.47
7	9	5	120–145	7	1.7	var
8	8	var	120–145	var	7.4	0.47
9▲	8	0	120–145	5	var	0.47
9■	8	10	120–145	10	var	0.47
9◆	8	20	120–160	13	var	0.63
10◆	8	0	120–140	6	7.4	var
10■	8	20	120–160	13	17.7	var
11◆	9	5	120–145	7	1.7	var
11■	9	5	120–150	7	30	var

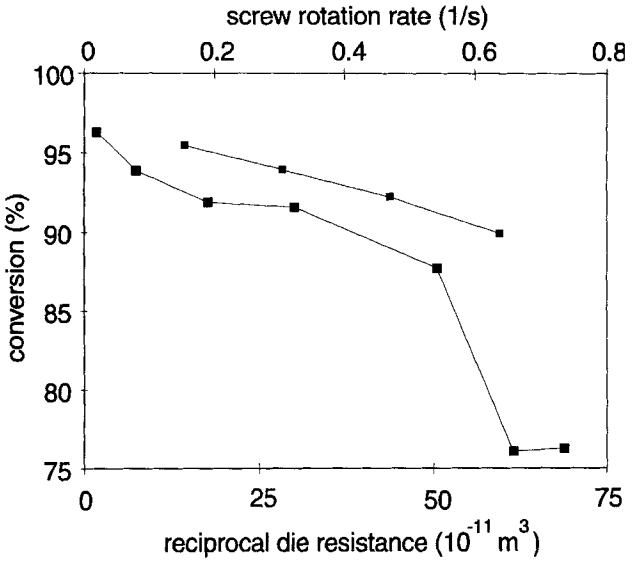

Fig. 4. The influence of the die resistance (■) and screw rotation rate (◆) on the conversion. The extruder settings are listed in Table 3.

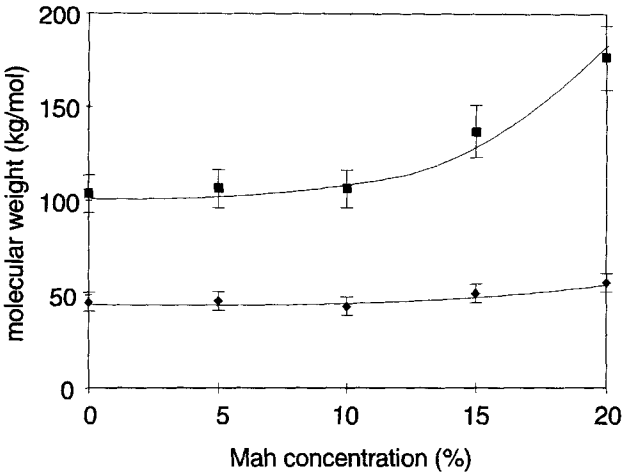

Fig. 5. The influence of Mah on the molecular weight of the polymer (■ M_w, ◆ M_n).

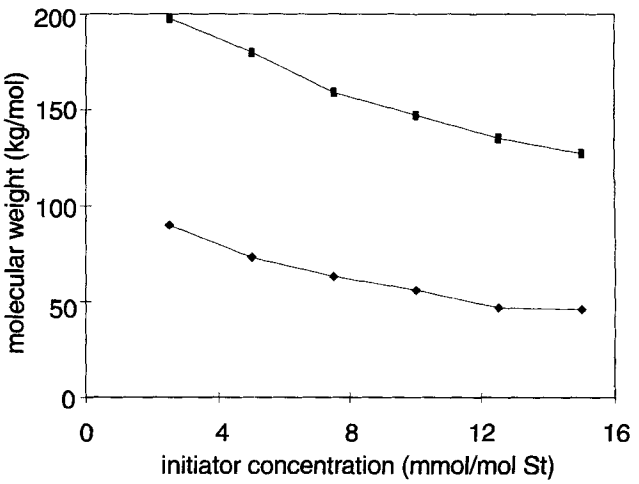

Fig. 6. The influence of the initiator concentration on the molecular weight (■ M_w, ◆ M_n).

polydispersity M_w/M_n increased from 2.4 to 3.6 when more Mah was added. These experiments indicate that the amount of Mah added to the mixture is a tool to adjust the molecular weight of the polymer formed.

The Influence of the Initiator Concentration and Extrusion Parameters on the Molecular Weight of the Polymer

A real tool to adjust the molecular weight of the polymer is the initiator concentration (*Equation 4*). *Figure 6* shows the effect of the initiator concentration on the molecular weight. The extruder was operated under standard conditions. It can be seen that the molecular weight was strongly influenced by the initiator concentration, but the influence was less than expected theoretically. Comparable results were obtained for the copolymerization of St and BMA (17). The ability of St to create radicals itself accounts probably for the smaller influence, since it produces extra radicals. It should be noted that the conversion of the product that left the extruder decreased with decreasing initiator concentration. When 2.5 mmole initiator per mole styrene was added to the mixture, the conversion became 77%, while with a higher initiator concentration, a conversion of 95% could be obtained. In summary, the initiator concentration is a rather pow-

erful tool to adjust the molecular weight of the polymer, but it should be kept in mind that the conversion is influenced by the amount of initiator added to the monomer mixture.

A change in extruder parameters, such as die resistance and screw speed, also influences the molecular weight of the polymer formed. The most reasonable explanation is that the material in the extruder undergoes another thermal treatment when an extruder parameter is changed, owing to the temperature profile along the barrel of the extruder. Hornsby (7) suggested that also the amount of shear influences the molecular weight. Although Hornsby found a very strong influence on the molecular weight in the case of polyamide 6, in radical polymerizations the influence is rather weak and often unpredictable (*Figure 7*, Reference 8). It can be concluded that a useful tool to influence the molecular weight of the polymer is the initiator concentration and not the extruder parameters, such as screw speed. In another study (17), it was found that the conversion after pre-polymerization and the temperature profile over the extruder were also good instruments to adjust the molecular weight. The influence of Mah was discussed in the previous section.

With the tools described, a minimum weight average molecular weight of 80 kg/mol (P = 2.3) and a maximum of 190 kg/mol (P = 2.8) was obtained for the St-BMA copolymer. When 20% Mah was added, a maximum of 230 (P = 3.5) could be obtained. As already stated, these molecular weights are relative molecular weights, and therefore a slight underestimation of the real molecular weights.

The Effect of Mah on the Process of Reactive Extrusion

The substitution of a certain part of BMA by Mah influenced the process of reactive extrusion strongly. *Figure 8* shows the effect of Mah on the maximum throughput of the extruder. The extruder operated under standard conditions. The maximum throughput was obtained if the extruder was fully filled with liquid or if the conversion became lower than the required conversion of 95%. We could obtain this conversion under standard conditions, except for the St-BMA copolymer. The conversion in that situation was at most 94%. The increase in throughput was larger than the increase in throughput because of an increased polymer melt viscosity (13). Therefore, it was concluded not only that the polymer melt viscosity is important, but that also an increase in the polymerization rate of the monomer mixture enlarges the working domain.

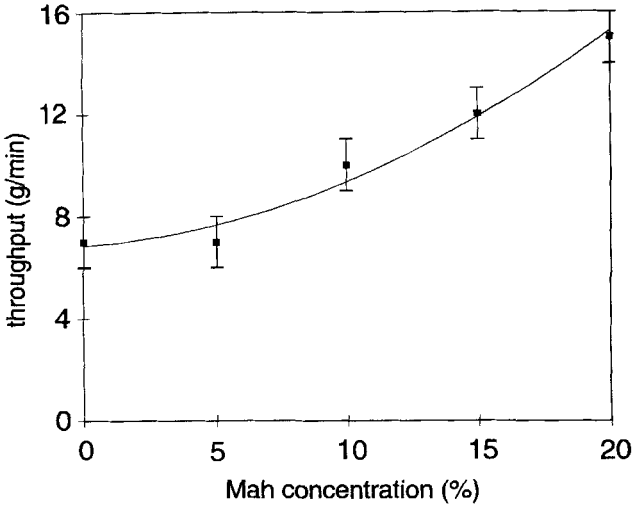

Fig. 8. The influence of Mah on the maximum throughput.

Figure 9 shows the effect of the die resistance on the conversion of the product that leaves the extruder. In these experiments, the extruder was operating under standard conditions, but when 20% Mah was added, the steep temperature profile was applied. The throughput was 7 g/min when 0% Mah was added, 10 g/min when 10% Mah was added, and 13 g/min when 20% Mah was added to the reaction mixture. It can be

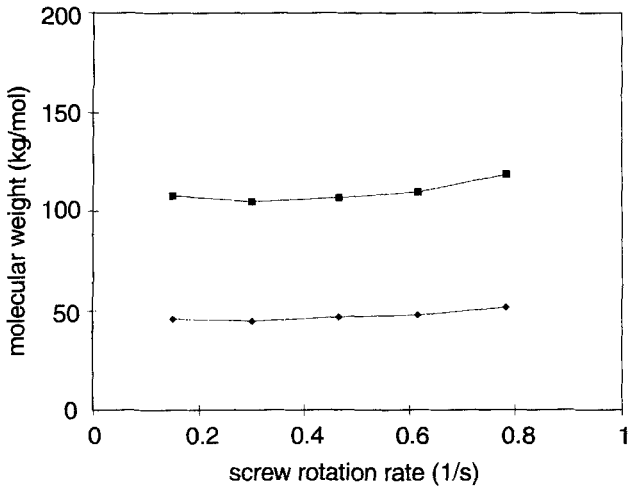

Fig. 7. The influence of the screw rotation rate on the molecular weight (■ M_w, ◆ M_n).

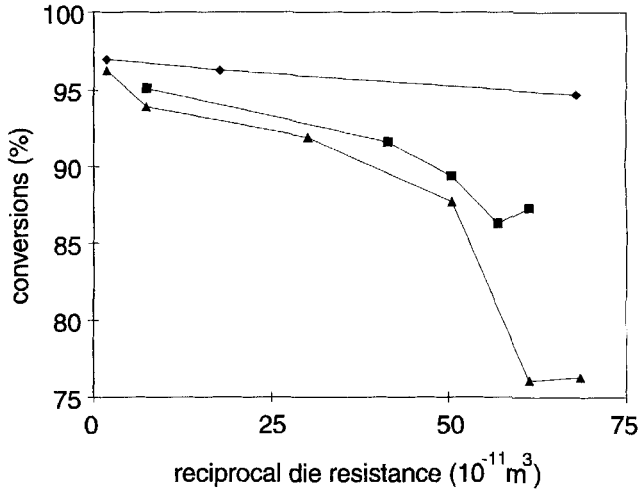

Fig. 9. The influence of the die resistance on the conversion (◆ 20% Mah, ■ 10% Mah, ▲ 0% Mah).

seen that the addition of Mah stabilized the process, since the influence of the die resistance decreased at higher Mah contents. The effect of stabilizing was even enhanced when the larger throughput at higher Mah concentrations was taken into account, since at a larger throughput a stronger effect of the die resistance was expected.

Figure 10 shows the effect of the screw rotation rate on the conversion. For the St-BMA-copolymer a decrease in conversion was observed. When Mah was added to the reaction mixture, the dependence of the conversion on the screw rotation rate diminished. This means that the magnitude of the effect of the screw speed depended also on the material that is in the extruder.

The magnitude of the effect of screw rotation rate was also influenced by the die resistance. At a high die resistance, a change of screw rotation rate hardly influenced the conversion, while at a low die resistance, the loss of conversion was significant when the screw speed was increased (*Fig. 11*). This effect could be explained as follows. The maximum conversion that could be obtained in extruder polymerizations turned out to be about 97%. At the high die resistance, this conversion was obtained. Because of the high die resistance, the residence time was larger than the reaction time needed for a conversion of 97%. A decrease in residence time due to an increase in screw rotation rate hardly influenced the conversion, because the residence time was still larger than the reaction time needed. At the low die resistance, the maximum conversion could not be obtained. The maximum conversion was 92% at a screw rotation rate of 9 rpm. This means that the monomer mixture was still able to polymerize and the residence time was in fact too short to obtain the conversion of 97%. In this situation, a decrease in residence time due to an increased screw speed resulted in a decrease in conversion. Why the conversion remained constant when the screw speed was varied between 19 and 39 rpm is not quite clear yet. This effect, a constant conversion, lower than the maximum conversion, at varying the screw speed was also observed by Ganzeveld (5) and Jongbloed (8).

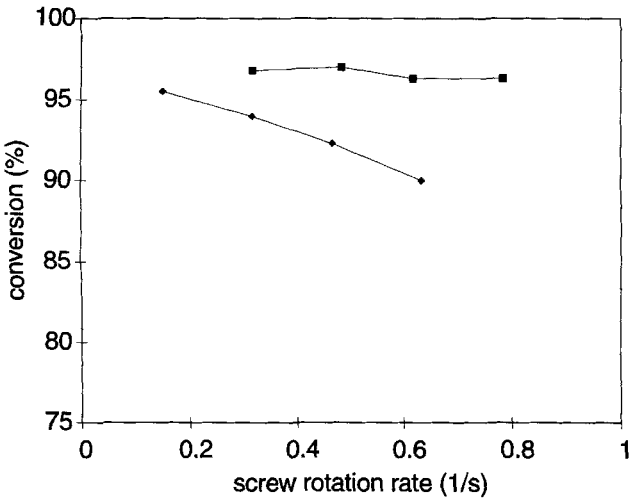

Fig. 10. The influence of the screw rotation rate on the conversion (■ 20% Mah, ◆ 0% Mah).

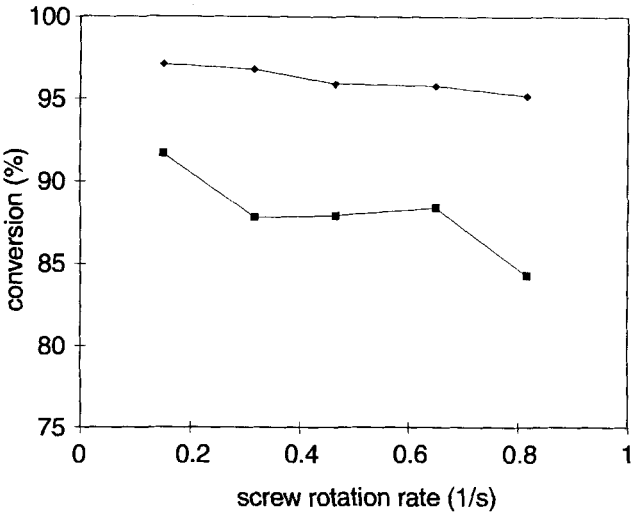

Fig. 11. The influence of the screw rotation rate at high (◆) and low (■) die resistance.

DISCUSSION OF THE RESULTS: A NEW THEORY FOR REACTIVE EXTRUSION

A new theory for the process of reactive extrusion will be discussed in this section. This theory describes qualitatively the polymerization in a closely intermeshing counter-rotating twin-screw extruder. The theory was developed because the most advanced theory so far (5) fails in several important situations. Two of the main cases will be discussed below.

The first case is the influence of the screw rotation rate. The interaction diagram predicts a decrease in conversion when the screw speed is increased, due to a decrease in residence time. *Figure 10* shows that a change in screw rotation rate hardly influences the conversion when 20% Mah is added to the reaction mixture. It can be concluded that an increase in screw rotation rate does not always lead to a decreased conversion. Sometimes, a constant conversion can also be obtained when varying the screw speed. The second case concerns the throughput. The interaction diagram conceives the throughput as primary parameter, just as in normal extrusion processes. However, in reactive extrusion, the maximum throughput will always be lower than the throughput in normal extrusion processes (*Fig. 8*). Moreover, *Fig. 8* shows that the maximum throughput is dependent on the polymerization rate of the reaction mixture in the extruder.

In addition to the cases discussed above, the interaction diagram does not take into account several other aspects. The first is the fact that the magnitude of influence of the extruder parameters is dependent on the reaction mixture in the extruder (*Figs. 9* and *10*). The second is the fact that the magnitude of influence of the extruder parameters is dependent on the other extruder parameters (*Fig. 11*). A higher die

resistance leads to a decreased dependence on the screw rotation rate.

To explain the results better, a new theory has been developed. The main idea behind the theory is the existence of an amount of nonreactive material before the die (*Fig. 12*). This material can be nonreactive because of lack of monomer (100% conversion) or lack of initiator, or because the polymerization had reached thermodynamic equilibrium (18). When a plug of this material is present in the last part of the extruder, the process of reactive extrusion will be rather insensitive to changes in extruder variables, such as screw speed and die resistance. The reason is that the material cannot change any further after complete reaction. The theory can be expanded by stating that the bigger the size of the plug of material, the more insensitive the reactive extrusion process is for any changes or disturbances. It should be noted that this plug of material is not the same as fully filled length; this plug is a part of that length. If the plug is not present, which means that the material that leaves the die is still reacting, the traditional theory, as given in the interaction diagram, can be applied.

The die resistance seems to be the most important extruder parameter, as it is the most powerful tool to create a plug of completely reacted material. For an optimal use of the extruder, one should choose a die resistance that results in a plug of completely reacted material of minimal size. This die resistance can be defined as the minimum die resistance (MDR). If a die resistance is applied that is larger than the MDR, the amount of mechanical energy added to the reacting material will be unnecessarily high, as a result of which unnecessary degradation can occur. Besides, when part of the extruder is occupied by nonreacting material, the volume of the extruder is not used effectively. A too low die resistance has a consequence that the required conversion will not be achieved. However, it should be noted that the application of the MDR leads to an extrusion process that is very sensitive to disturbances. For stability reasons, one should apply a die resistance that is somewhat higher than the MDR.

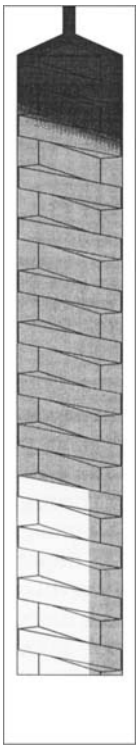

Fig. 12. Situation in which a plug (the darkest part) of completely reacted material is present before the die. This plug is part of the fully filled length.

The MDR is different for each monomer mixture. As can be seen in *Fig. 9*, the amount of Mah determines the lowest die resistance (MDR) at which conversion of 95% can be still obtained. Obviously, a faster polymerization needs a lower die resistance for sufficient conversion. From experiments in which the polymer melt viscosity is increased by crosslinking (15), we can conclude that the MDR is also influenced by the polymer melt viscosity. Since the polymerization rate and polymer melt viscosity are dependent on the temperature applied, the MDR will also depend on this temperature. The influence of the screw rotation rate is small compared with that of the die resistance. As a result, the MDR will be slightly influenced by the screw rotation rate.

The interaction diagram states that the throughput can be adjusted at every value in the normal working domain of the extruder. Within this working domain, the throughput is more or less a primary parameter that is limited by the maximum throughput, which can be obtained in the extruder. In reactive extrusion processes, however, the throughput will always be limited, as will be explained below.

Suppose that we want to produce a certain amount of polymer. The die resistance needed is given by the MDR. This die resistance, together with the throughput and viscosity, determines the pressure at the die entry (9, 13). If the extruder is fed with pure polymer, the pressure will increase linearly with the fully filled length, as indicated by line 1 (*Fig. 13*) for the ideal iso-viscous situation. The fully filled zone occupies only part of the extruder, so the throughput can be varied freely in a quite large operating window. If the extruder is fed with monomer, the pressure profile indicated by curve 2 will be obtained, provided that the throughput is similar and the conversion of the monomer is 100%, resulting in an identical polymer as above. Since the product that leaves the extruder is similar for situation 1 and 2, the slope of the pressure profile at the die entry should be identical. Owing to the decreased viscosity in the direction of the feed zone, the slope will decrease, which results in a larger fully filled length. In the situation indicated in *Fig. 13*, the extruder is nearly fully filled, which implies that the throughput cannot be increased any more. So, in reactive extrusion, the maximum throughput is much smaller than the throughput in normal extrusion processes. For example, the maximum throughput described in this thesis was around 2% to 4% of the theoretical throughput. Even for a very fast polymerization as performed by Jongbloed (8), the maximum throughput was limited to 10% of the theoretical

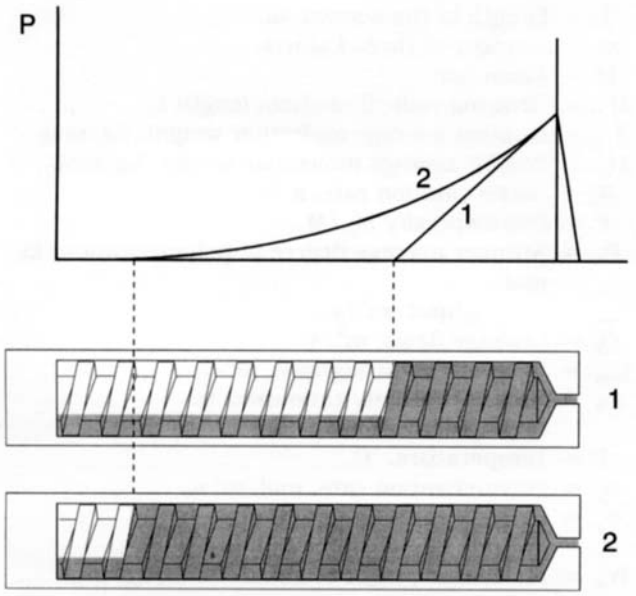

Fig. 13. Pressure profiles along the extruder (1: normal extrusion process, 2: reactive extrusion).

throughput. Therefore, the throughput can better be considered as an extrusion variable rather than as a parameter that can be adjusted freely. However, it will be clear that when the polymerization is very fast, the limitation in throughput will be less troublesome.

By means of the theory described above, we can optimize the reactive extrusion process, as indicated in *Fig. 14*. The screw speed should be adjusted at a moderate speed; the temperature profile is especially in large extruders difficult to control, and sometimes it should be used to adjust the molecular weight of the polymer formed. This means that the temperature of the material in the extruder is not a real process parameter. The same holds for the initiator concentration. With this in mind, the diagram shown in *Fig. 14* is developed. It optimizes experimentally the process of reactive extrusion by looking for the lowest possible die resistance, combined with the maximum throughput, resulting in a high (more than 95%) conversion.

CONCLUSIONS

The closely intermeshing counter-rotating twin-screw extruder is a suitable polymerization reactor for

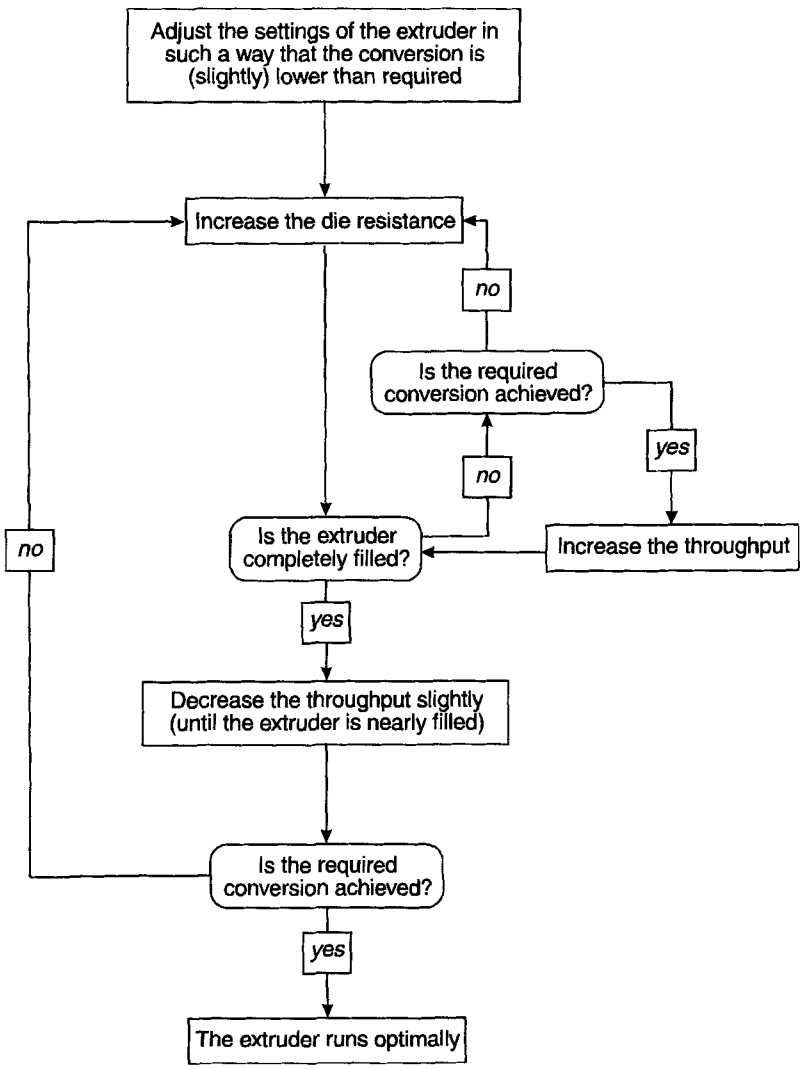

Fig. 14. Optimization scheme for reactive extrusion.

the copolymerization of St-n-BMA and the terpolymerization of St-BMA-Mah. However, the St-BMA copolymerization is rather difficult to perform. The die resistance has to be high and the temperature profile cannot be set freely. The addition of Mah led to a faster polymerization and a more viscous polymer melt. As a result of these two effects, the extrusion process became more stable, which meant that the dependence on extruder parameters such as die resistance was diminished. Besides, the maximum throughput could be increased significantly. It can be concluded that a faster polymerization results in a wider operation window of the extruder.

The molecular weight of the polymer formed is mainly dependent on product parameters such as initiator concentration and Mah content. The dependence on extruder parameters, except for the temperature profile, is quite small and seems unpredictable. The initiator concentration influences the molecular weight, but the influence is somewhat smaller than expected. The addition of Mah leads to a higher molecular weight.

The theory developed in this article is very useful in optimizing the process of reactive extrusion. The theory states that for a stable reactive extrusion process, the existence of a plug of completely reacted material just before the die is very important. If this plug is not present, the required conversion will not be achieved; if the plug is too small, a small disturbance in extruder parameters can lead to instabilities in the process. A too big plug leads to an unnecessary energy input into the material. The formation of the plug depends on either the extruder parameters and product properties, such as polymerization rate and polymer melt viscosity.

The limitation in throughput in reactive extrusion, when compared with normal extrusion processes, can be explained by the large change in viscosity during the polymerization. The limitations are less troublesome when the extruder is used as polymerization reactor for fast polymerizations.

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NOMENCLATURE

D = Diameter of the screws, m.
F_a = Mole fraction of component A in the polymer.
I = Initiator.
K = Reciprocal die resistance, m^3.
k_{12} = Propagation rate constant growing polymer A with component B, m^3/mol s.
k_d = Initiator decomposition rate constant, 1/s.
k_p = Propagation rate constant, m^3/mol s.
k_t = Overall termination rate, m^3/mol s.
L = Length of the screws, m.
m = Number of thread starts.
M = Monomer.
M_i = Growing radical of chain length i.
M_n = Number average molecular weight, kg/mol.
M_w = Weight average molecular weight, kg/mol.
N = Screw rotation rate, s^{-1}.
P = Polydispersity M_w/M_n.
P_n = Number average degree of polymerization, kg/mol.
Q = Throughput, m^3/s.
Q_l = Leakage flows, m^3/s.
Q_{th} = Theoretical throughput, m^3/s.
r_{12} = Binary reactivity ratio used in terpolymerization.
T = Temperature, °C.
v_p = Polymerization rate, mol/m^3 s.
v_y = Velocity in the y-direction, m/s.
V_c = Volume of a C-shaped chamber, m^3.
W_m = Molecular weight of monomer M, kg/mol.
η = Viscosity, Pa s.
η_s = Apparent viscosity, Pa s.
$\dot{\gamma}$ = Shear rate, 1/s.
τ_{xy} = Shear stress, Pa.
[ ] = Concentration, mol/m^3.

REFERENCES

1. R. D. Bayley, U.S. pat. 4,148,741 (1979) (to Xerox Corp.).
2. M. V. Joshi and D. Mukesh, *J. Appl. Polym. Sci.*, **50,** 75 (1993).
3. J. R. Ebdon, C. R. Towns, and K. Dodgson, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **C26,** 523 (1986).
4. B. Klumperman, PhD thesis, University of Eindhoven, The Netherlands (1994).
5. K. J. Ganzeveld and L. P. B. M. Janssen, *Can. J. Chem. Eng.*, **71,** 411 (1993).
6. W. Michaeli, H. Höcker, U. Berghaus, and W. Frings, *J. Appl. Polym. Sci.*, **48,** 871 (1993).
7. P. R. Hornsby, J. F. Tung, and K. Taverdi, *J. Appl. Polym. Sci.*, **53,** 891 (1994).
8. H. A. Jongbloed, R. K. S. Mulder, and L. P. B. M. Janssen, *Polym. Eng. Sci.*, **35,** 587 (1995).
9. L. P. B. M. Janssen, *Twin Screw Extrusion*, Elsevier Sci. Publ. Company, Amsterdam (1978).
10. K. J. Ganzeveld, J. E. Capel, D. J. van der Wal, and L. P. B. M. Janssen, *Chem. Eng. Sci.*, **49,** 1639 (1994).
11. C. H. Bamford and C. F. H. Tipper, *Comprehensive Chemical Kinetics*, **14a** (Free radical polymerization), Elsevier Publishing, Amsterdam (1976).
12. G. Schmidt-Naake, H. Schmidt, B. Litauszeki, and M. Noriega, *Polymer Reaction Engineering*, p. 230, Reichert/Geiseler, VCH Berlin (1989).
13. A. J. van der Goot, R. Hettema, and L. P. B. M. Janssen, *Polym. Eng. Sci.*, this issue.
14. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd Ed., J. Wiley, New York (1989).
15. D. C. Blackley and H. W. Melville, *Makromol. Chem.*, **18,** 16 (1956).
16. A. M. North and D. Postlethwaite, *Polymer*, **5,** 237 (1965).
17. A. J. van der Goot, S. A. Klaassens, and L. P. B. M. Janssen, *SPE ANTEC Tech. Papers*, **41,** 232 (1995).
18. F. S. Dainton, F. R. S. Ivin, and K. J. Ivin, *Quarterly Reviews*, **12,** 61 (1958).

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